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R. W. Hufferd

The Application of Victor Meyer's  
Esterification Law



THE APPLICATION OF VICTOR MEYER'S ESTERIFICATION  
LAW TO NEIGHBORING-XYLIC ACID AND  
ITS REDUCED DERIVATIVES

BY

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A. B. Washington University, 1915

M. A. University of Illinois, 1917

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

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THE GRADUATE SCHOOL

May 10 1920

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY RALPH WILLIAM HUFFERD  
ENTITLED THE APPLICATION OF VICTOR MEYER'S ESTERIFICATION  
LAW TO NEIGHBORING XYLIC ACID AND ITS REDUCED DERIVATIVES  
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
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## /

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# BIELIOGRAPHY

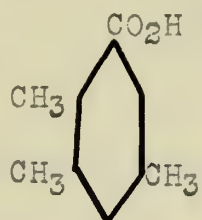
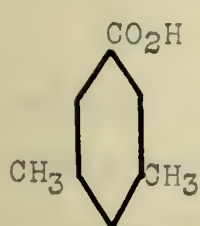
1. Ber., 27, 510 (1894)
2. Ber., 27, 1585 (1894)
3. Ber., 27, 3146 (1894)  
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 Ber., 29, 830, 839, 1397 (1896)  
 Ztech. Phys. Ch. 16, 385 (1895)  
 Ztsch. Phys. Ch. 24, 219, 221 (1897)
4. Monatsch. f. Ch. 18, 643 (1897)  
 Ber., 28, 2535 (1895)
5. Jr. Am. Ch. Soc. 30, 1895, 1908 (1908)
6. Jr. Am. Ch. Soc. 30, 1908 (1908)
7. Ber., 33, 2022 (1900)
8. Zts. Phys. Ch. 21, 154 (1896)
9. Am. Ch. Jr. 20, 807 (1898)
10. Jr. Am. Ch. Soc. 39, 2718 (1917)
11. Ann. 272, 269 (1893)
12. Ber., 45, 1475 (1912)
13. Ber., 49, 2294 (1916)
14. Ber., 27, 2833 (1894)
15. Comp. Rend. 154, 924 (1912)  
 Comp. Rend. 156, 426, 752 (1913)
16. Jr. Am. Ch. Soc. 34, 59 (1912)
17. Friedlander 1912-14, 206
18. Ber. 24, 2216 (1891)  
 Soc. 75, 166 (1899)
19. Jr. Am. Ch. Soc. 42, 531; 43, 205, 212; 44, 162, 183
20. Jr. Am. Ch. Soc. 36, 2268 (1914)



## I. HISTORICAL

Having need of the methyl ester of mesitylene carboxylic acid, Victor Meyer attempted to prepare it by dissolving the acid in methyl alcohol, saturating with dry hydrochloric acid, and allowing the solution to set for twelve hours. (1) He was surprised to find that only 9% was esterified. As benzoic acid will yield 97% of the ester by like treatment, he concluded that the low yield was due to the accumulation of methyl groups.

In order to clear up the point, he studied several substituted benzoic acids.



gave yields of over 80% of the ester.



with like treatment, gave a 96% yield.

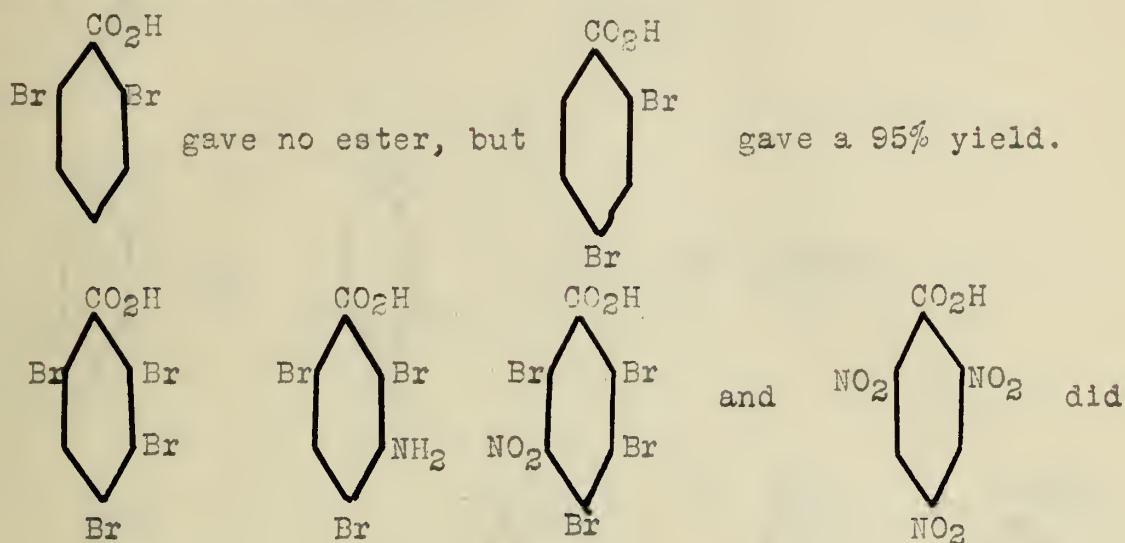
These results showed clearly that it was not the number, but rather the position of the substituting groups which produced the effect observed. Meyer made the statement, "Aus den vorliegenden Versuchen folgt das uberraschende Factum, das in der That diejenigen trisubstituirten Benzoesauren, welche die Substituenten in symmetrischer (1,3,5) Stellung enthalten, durch Methylalkohol und Salzsaueregas nur in ganz beschrankten Maasse esterfiziert werden konnen, wahrend ihre Isomeren und alle ihre Analogen





der Esterficirung keinerlei Schwierigkeiten entgegen setzen".

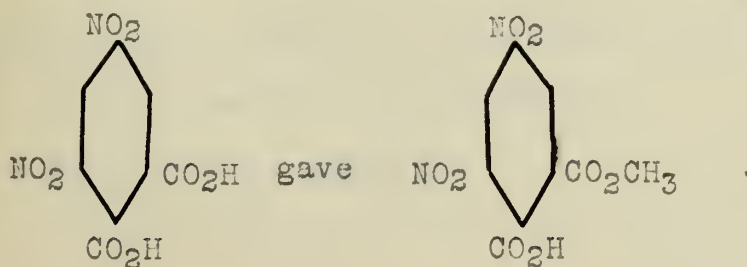
He continued his study of polysubstituted benzoic acids (2) with quite definite results.

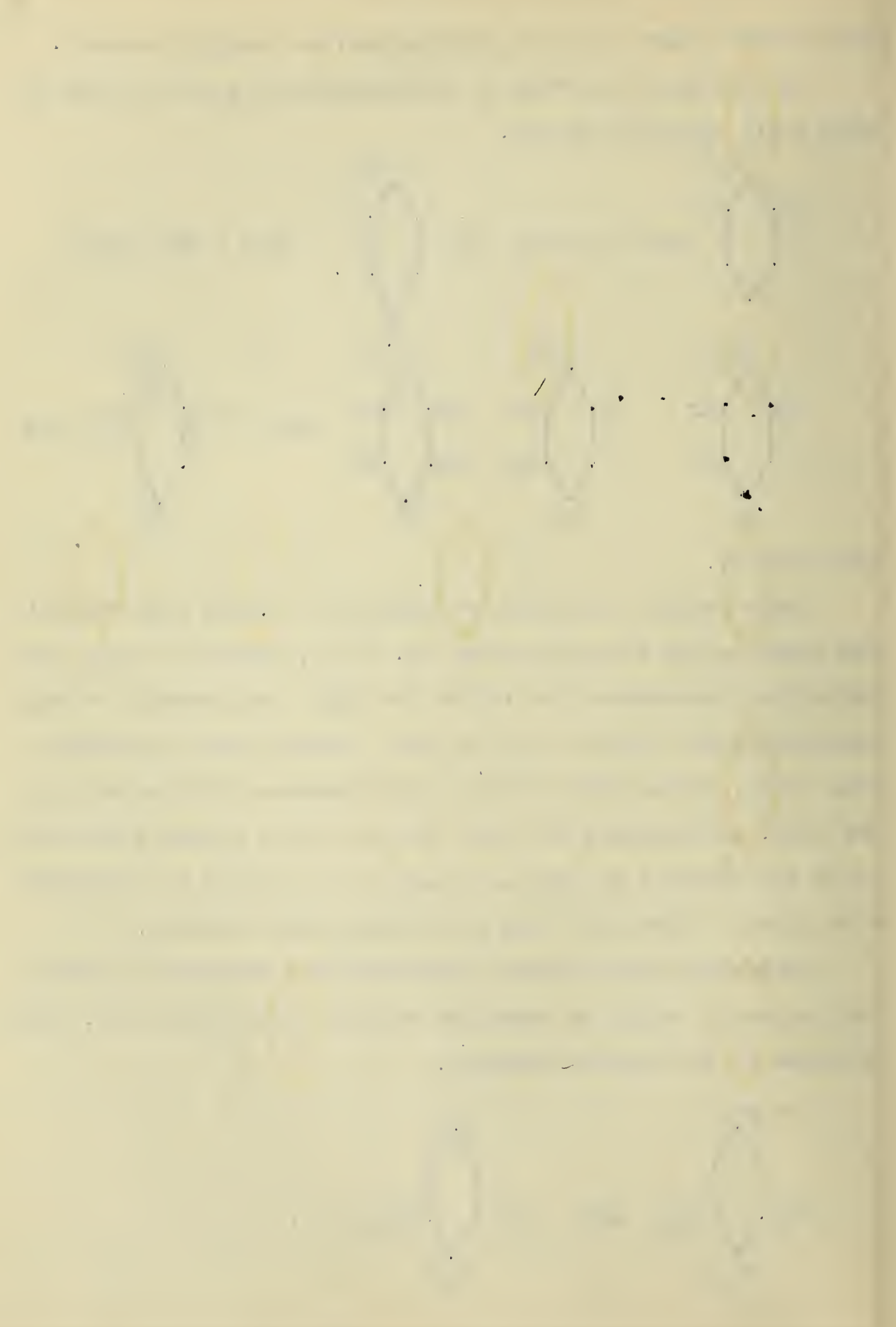


not esterify.

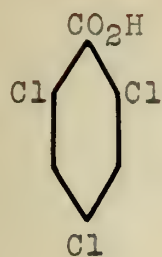
These results led Meyer to formulate a second rule which is now known as his Esterification Law. It is, "Sobald in einer substituirten Benzoesaure die beiden dem  $\text{CO}_2\text{H}$  benachbarten H-Atome durch Radicale, wie Br,  $\text{NO}_2$ ,  $\text{CH}_3$  etc., ersetzt sind, resultirt eine Saure, welche durch Alkohol und Salzsäure nicht esterficirbar ist". He developed the idea that the ortho groups merely cover up the carboxyl to such an extent as to prevent its collision with alcohol molecules, thus preventing esterification.

Following this statement, Meyer and his students (3) made a very extensive study of compounds which are affected by it. Below are some of the results obtained.

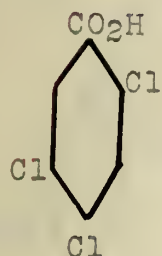








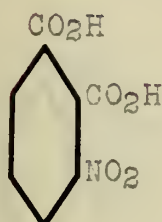
gave no ester.



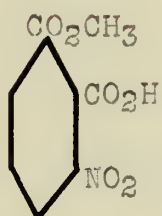
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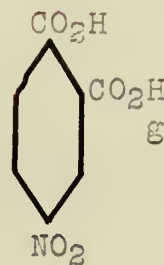
esterified normally.



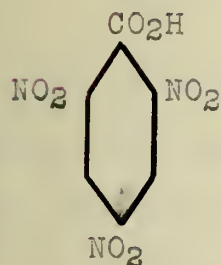
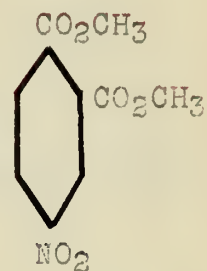
gave



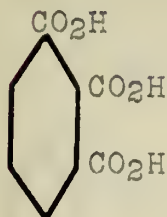
, but



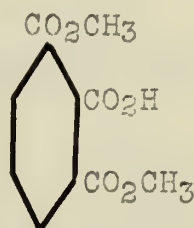
gave



was easily esterified by the silver salt method, but gave no ester when heated with methyl alcohol for thirty days, hydrochloric acid being passed into the solution.



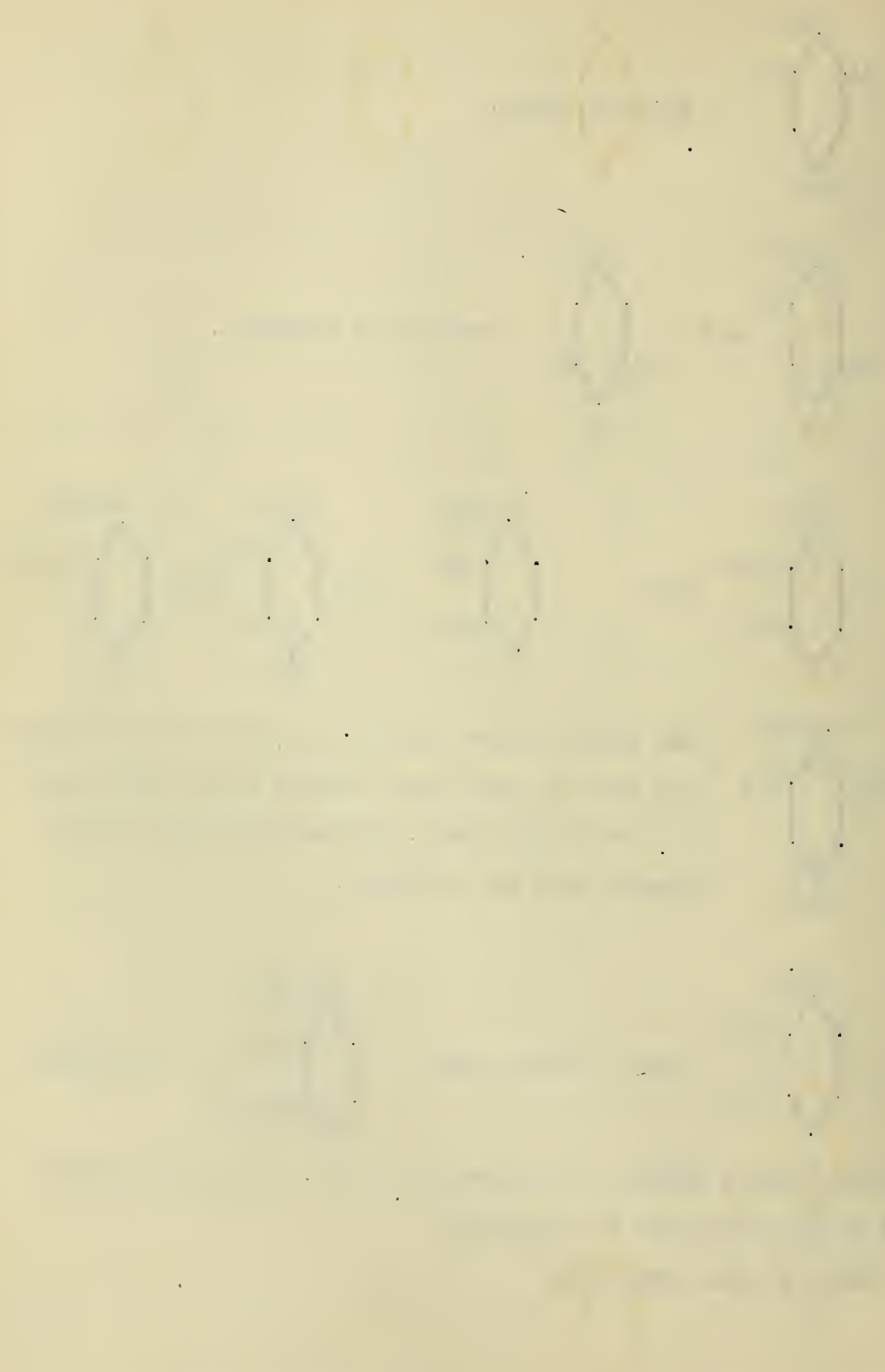
gave, in the cold,

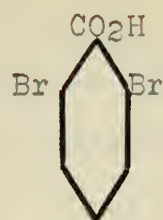
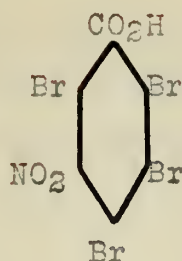
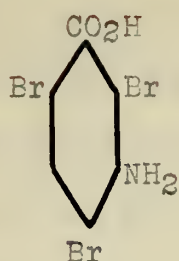
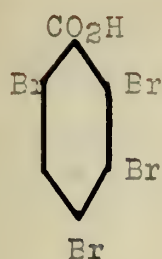


, but when

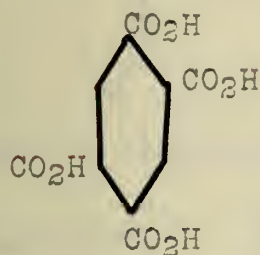
heated, a small amount of the neutral ester. This was probably due to the formation of anhydride.

None of the compounds;

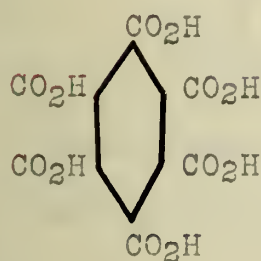




gave more than 2% yields of ester.



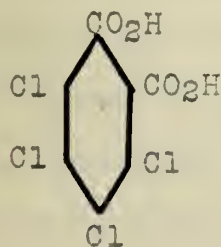
gave the neutral ester.



, even with prolonged heating, refused to esterify.

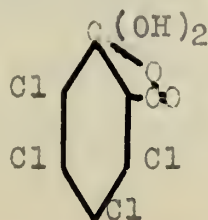
The rule seems to hold very well for almost all di-ortho-substituted aromatic acids, except where the ortho positions are filled by hydroxyl groups. In such compounds the esterification in the cold is greatly slowed down, but if heated, the yields are decreased.

One of the most outstanding exceptions to Meyer's law is

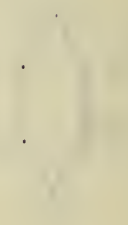
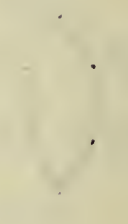
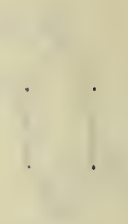
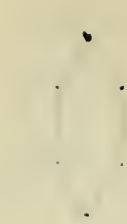
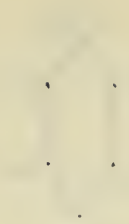


, which yields the acid ester. Meyer explained the unusual result by assuming for the acid

the formula,



, which he got from the formula ad-



vanced to explain the properties of phthalyl dichloride.

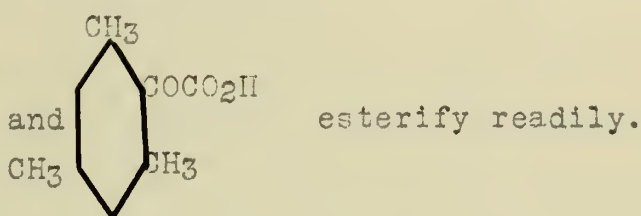
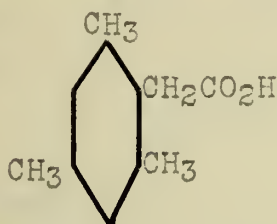
A strong argument for the steric hindrance idea is found in the action of substituted acids with the carboxyl removed from the ring by at least one atom.



is much more readily esterified than is benzoic acid itself, seeming to indicate that the ortho hydrogen atoms themselves

exert a hindering effect.

Similarly,



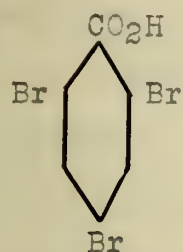
Wegscheider (4) tried to esterify 2,4,6,tribrom benzoic acid by heating 2 grams with 25cc.methyl alcohol and 1.75cc. sulphuric acid for 4 1/4 hours. After standing twenty hours longer at the temperature of the laboratory, no ester was found. He repeated the experiment, using 20cc. concentrated sulphuric acid. By heating for 4 1/4 hours and then letting stand for 13 1/2 hours, he obtained a 12% yield of the ester. This method was, of course, much more violent than that used by Meyer in his work. Wegscheider objected to the steric hindrance view and declared that the effect is due to a state of tension within the molecule.

The most antagonistic critic of Meyer's steric hindrance idea is M.A.Rosanoff (5). He and his co-workers carried out several esterification experiments in which the acid was heated with ethyl alcohol in a sealed tube without the addition of any mineral acid. Most of the trials were made at the temperature of boiling

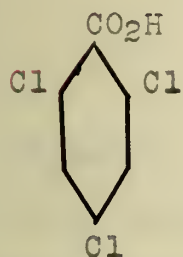




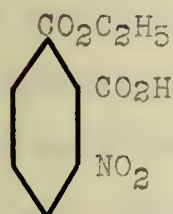
aniline, and for a much longer time than is ordinarily employed for esterifications. Some of these results are given below.



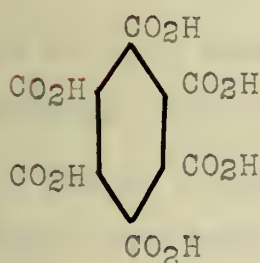
was heated for 100 hours at 216° with 20 parts of absolute alcohol, yielding 100% ester.



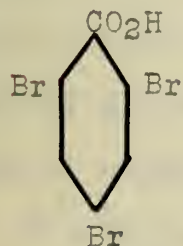
gave 73% in 97 hours at 183°.



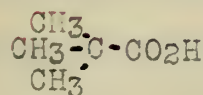
gave 91.5% of neutral ester in 63 hours at 183°.



gave 60.5% of neutral ester in 96 hours at 183°.



gave the ester when heated for a long time in an open vessel.



gave 89% ester in 63 hours at 89°.





The speed of esterification of several acids was determined at the temperature of boiling aniline, and the velocity constants computed.

| Acid                   | Equilibrium K | Velocity K |
|------------------------|---------------|------------|
| Acetic                 | 4.0           | .00061     |
| Trichlor benzoic 2,4,6 | .105          | .31        |
| Tribrom benzoic 2,4,6  | .42           | .088       |
| " " 2,3,5              | .12           | .37        |
| " " 3,4,5              | .30           | .90        |
| Benzoic                | .40           | .63        |

From these results Rosanoff came to the conclusion that "di-ortho substituted aromatic acids, which are generally assumed to be unesterifiable, can be esterified quantitatively at higher temperatures, or even, by prolonged warming, at the temperature of the water-bath". He states the esterification law, "Aromatic acids with one or both positions next to the carboxyl occupied by substituting groups, combine with alcohols more slowly, though to no less extent, than acids otherwise substituted". He concludes further, "Our dynamic study proves that Victor Meyer's hypothesis of steric hindrance is untenable and thus, for the present, reduces the Esterification Law to the rank of an empirical rule of no theoretical and limited practical value. The hypothesis that the low rate of esterification is due to the mechanical interference of groups or atoms situated near the carboxyl in the molecule is untenable".

W.L. Prager (6) followed the method employed by Rosanoff, and determined the velocity constants of several substituted acetic acids. From his results he concluded, similarly to Rosanoff, that the steric hindrance idea is untenable.



Prager attempted a separation of benzoic and anthranilic acids by esterifying the mixture. He first let 10gr. benzoic in 200cc. absolute alcohol containing 3% hydrochloric acid stand at ordinary temperature for 23 days, and obtained an 86.5% yield of ester. When treated in a similar manner, anthranilic did not yield any ester. A mixture of 10 grams of each in 400cc. of alcohol gave over 6 grams of pure ethyl benzoate. His conclusion was that the method permits of separating mono-ortho substituted acids from other acids, though he does not believe the fact is due to steric hindrance.

Graebe (7) found that similarly to tetra chlor phthalic acid, 1,4,di chlor phthalic acid will give the acid ester on standing in ethyl alcohol containing hydrochloric acid, and a 16% yield of the neutral ester if boiled for seven hours.





## II. THEORETICAL

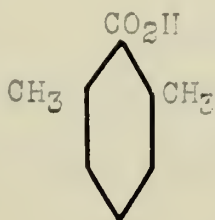
From the preceding resume of the literature it is evident that there are two distinct points of view from which a reaction may be considered. Meyer studied the qualitative aspect to draw his conclusions which he couched in quantitative terms. Rosanoff, following the belief of Bredig (8) that everything chemical must be considered quantitatively from the dynamic side, considers it useless to distinguish between difficult and easy reactions. According to him, no rule of any great value could be deduced from such a grouping, and no knowledge could be gained as to molecular structure by correlating such reactions.

Although Rosanoff refuses to give any consideration to Meyer's explanation of the hindrance being due to a blanketing effect, he very willingly accepts Wegscheider's idea that it is due to a condition of strain within the molecule induced by the substituting groups.

Without accepting entirely either of the above explanations but with a firm conviction that organic structures can be deduced from cumulative evidence of a qualitative nature and cannot be assigned numerical values, the present work was undertaken.

If Meyer's explanation is correct, the following results can be predicted.

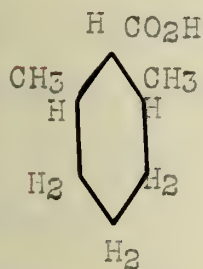
Neighboring xylic acid,



, should not esterify.



Hexahydro neighboring xylic acid,

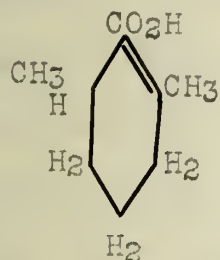


, has very much the same grouping as xylic, but is purely aliphatic in nature. Its three isomers would be expected to give different results, which might be predicted as follows: the one

with the grouping  $\begin{array}{l} -\text{C}-\text{CH}_3 \\ -\text{C}-\text{CO}_2\text{H} \\ -\text{C}-\text{CH}_3 \end{array}$  should not esterify; the second, with the

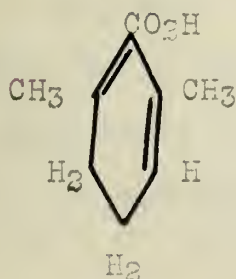
grouping  $\begin{array}{l} -\text{C}-\text{CH}_3 \\ -\text{C}-\text{CO}_2\text{H} \\ \text{CH}_3-\text{C}- \end{array}$ , would be expected to esterify with very poor yields; the third, which would have the grouping  $\begin{array}{l} \text{CH}_3-\text{C}- \\ -\text{C}-\text{CO}_2\text{H} \\ \text{CH}_3-\text{C}- \end{array}$ , would probably esterify easily.

$\Delta_1$  tetrahydro neighboring xylic acid, in which the carboxyl is in the same plane with only one methyl group,



, would not be expected to esterify with as much difficulty as xylic acid itself.

$\Delta_{1,5}$  dihydro neighboring xylic acid,



, of which the linkage of the carboxyl group is the same as in xylic acid, should not esterify easily.

The  $\Delta_3$  tetrahydro neighboring xylic acids from their similarity to the hexahydro acids, would be expected to behave in much the same manner.





## III DISCUSSION OF RESULTS

The results obtained in this study of neighboring xylic acid and its reduction products, agree quite well with the predictions based on Victor Meyer's Esterification Law.

| Acid                         | Predicted Esterification | Found |
|------------------------------|--------------------------|-------|
| Benzoic                      | quantitative             | 96%   |
| Xylic                        | none                     | 3.5%  |
| Hexahydro xylic              | poor to good             | 52%   |
| $\Delta_1$ tetrahydro xylic  | fair                     | 41%   |
| $\Delta_{1,5}$ dihydro xylic | none                     | 25%   |
| $\Delta_3$ tetrahydro xylic  | poor to good             | 75%   |

From this comparison of the results obtained with those predicted, it is evident that the Esterification Law cannot be applied quantitatively. However, the results offer strong evidence combatting Rosanoff's statement to the effect that the law is of little practical value.

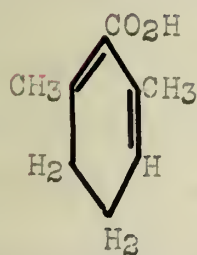
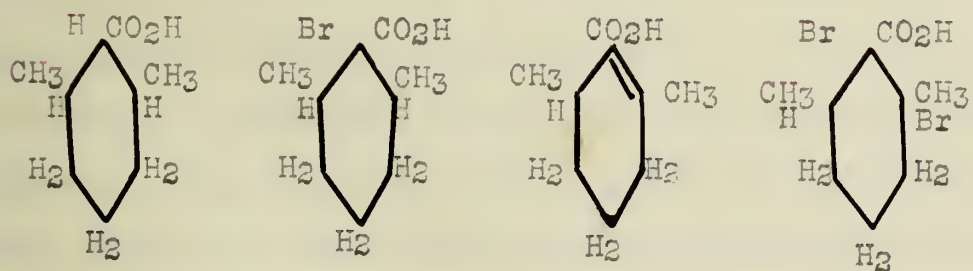
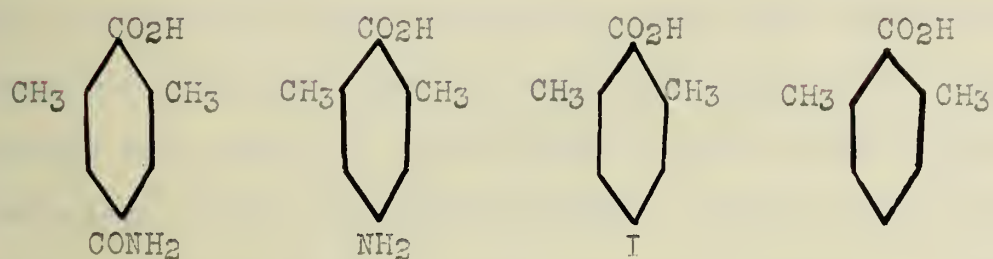
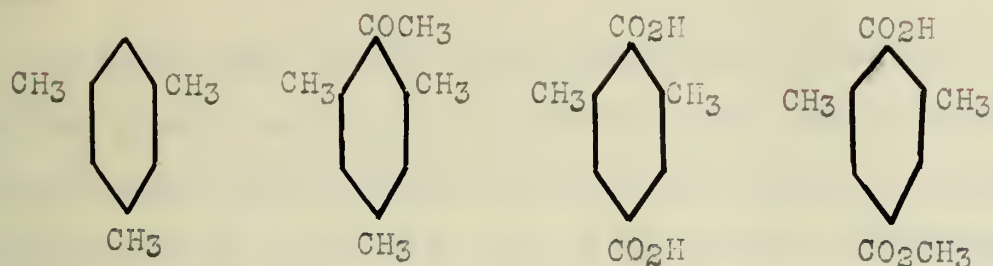
None of the results, in so far as the author can see, can be better explained than by the steric hindrance idea as advanced by Meyer.

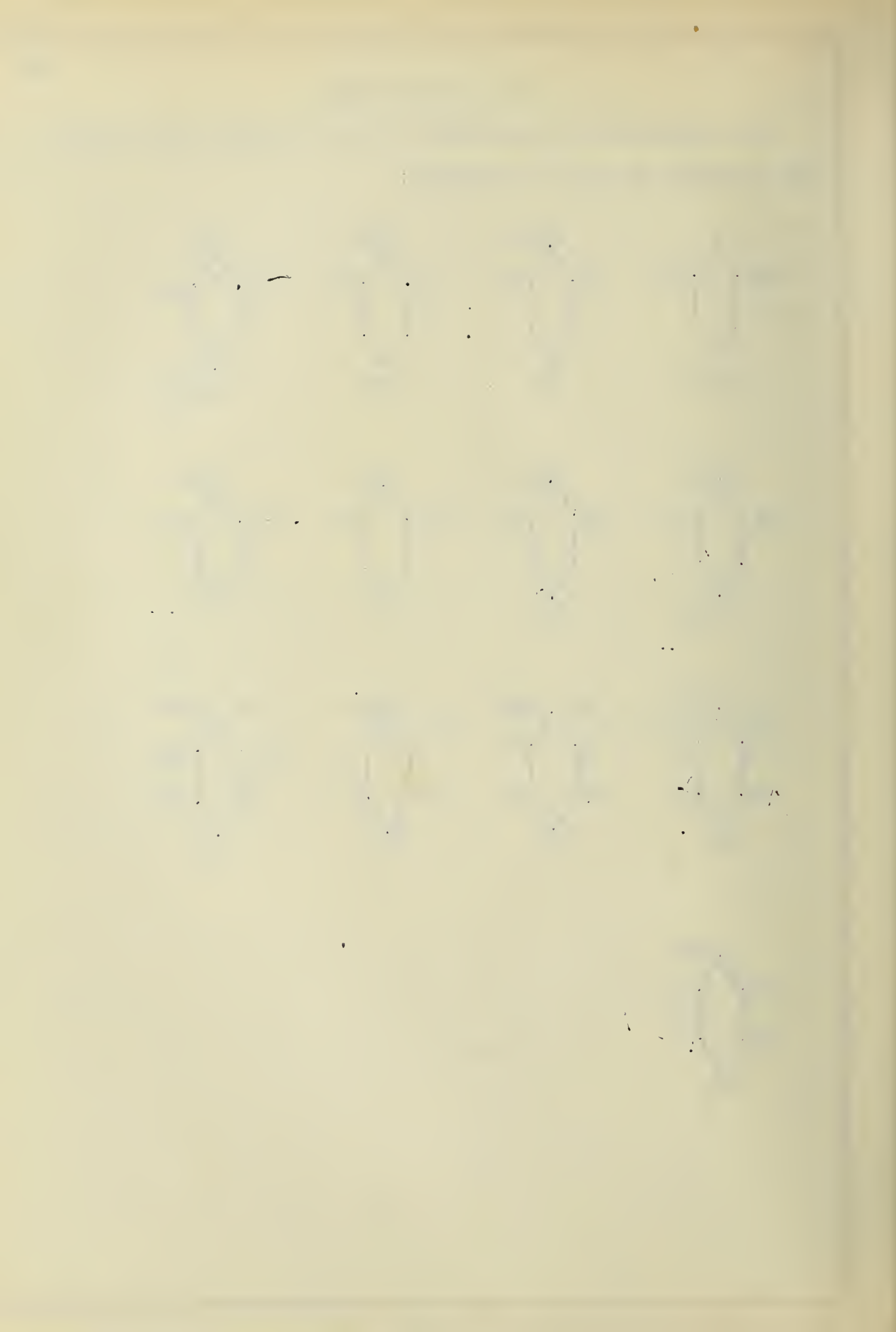
Due to the impure condition of the dihydro acid it is impossible to state definitely its relation to Victor Meyer's law. However, it undoubtedly yields less easily to esterification than does either the 1,2,tetrahydro acid or the hexahydro acid.



## IV EXPERIMENTAL

The preparation of materials for this problem was through the following series of compounds:







## Preparation of Mesitylene

The method of W.A.Noyes (9), modified somewhat to permit of making larger quantities, was used in the preparation of mesitylene.

To 2300 grams (5750cc.) of commercial acetone in a five-liter balloon flask, surrounded by ice and salt, and stirred vigorously with a motor-driven stirrer, were added 2100cc. of commercial sulphuric acid, at such a rate as to prevent the temperature from getting above 18°. This required over three hours. The stirring was continued for three hours more, and the mixture allowed to stand for 18 to 20 hours at room temperature. One third of the mixture was placed in a five-liter balloon flask, fitted to a long, large-bore, water-jacketed condenser. Using a free flame, the flask was heated so that the reaction became vigorous in about fifteen minutes. The flame was then turned low, and finally removed after three minutes. A rapid current of steam was then passed through the solution. After five minutes the the receiving flask was changed, and steam passed through until the distillate was about 700cc. During the last part of the distillation a low flame was applied. The first fractions of the three portions were placed in a large separatory funnel, and washed with caustic soda solution until the sharp odor had entirely disappeared. It was then washed with water. A small portion, which was emulsified with wash-water, was run into the container holding the batched second distillates. The second distillates were treated as the first except that the emulsion was broken by the addition of calcium chloride.

The combined oily portions were distilled up to 210°. This dis-



tillate was placed in a distilling flask, fitted to a condenser, and about ten grams of sodium added in small pieces. The flask was heated somewhat below the boiling-point of the contents for three hours. About two thirds of the material was distilled off, the residue cooled, the sodium removed, and the residue distilled up to  $210^{\circ}$ . The distillate was then fractionated through a Skinner column (10), the fraction  $162^{\circ}$ - $165^{\circ}$  being collected separately. The portion  $165^{\circ}$ - $185^{\circ}$  was batched with the low-boiling fraction, and the fractionation repeated. This was repeated until all of the mesitylene had been obtained.

The yield varied from 16% to 19% of the theory for the acetone used.

The method was varied in a great number of ways, but in no case was the yield as good as above.

Thinking that the mass relationship in mixing the acetone and sulphuric acid might be responsible for the low yield, the mixing was reversed by adding the acetone to the acid. The yield was very low.

In order to study the effect of temperature on the reaction, runs were made keeping the temperature below  $8^{\circ}$ , between  $10^{\circ}$  and  $15^{\circ}$ , and just below  $30^{\circ}$ . The yield was no better in either of the first cases and was worse in the last.

Seemingly contradictory results were obtained in one run in which no care was taken to keep the temperature low. The acetone was cooled under the tap, and the sulphuric acid added as fast as possible without volatilizing the acetone too greatly. The mixture was let stand at room temperature for three hours, and then warmed to  $60^{\circ}$  on the steam-bath, and let stand at room temperature for





three hours longer. Heat was applied, and steam passed in as soon as the reaction started. The flame was not removed at any time during the whole distillation. The yield was about 14%, almost no high boiling material being obtained.

It was found that unless the flame was removed or turned low as soon as the reaction slowed down, the yield went chiefly to high boiling products.

Distilling the reaction mixture in quantities of more than 2000cc. decreased the yield greatly.

Prepared by this method, the mesitylene boils at  $262^{\circ}$ - $265^{\circ}$  at 750mm. It does not turn dark after several months' standing.

#### Preparation of Acetomesitylene

To 255 grams of mesitylene, dissolved in a liter of dry carbon disulphide in a three-liter flask, were added 625 grams of freshly distilled acetyl chloride. 260 grams of anhydrous aluminum chloride were added in small portions over a period of two hours. During this time the flask was kept stoppered with a one-hole stopper. The mixture was then allowed to stand for a half hour, and finally poured into cracked ice. The disulphide layer was separated off, and the residue shaken out with 500cc. of carbon disulphide. The disulphide was distilled off from the combined extracts, and the residue distilled through a Skinner column. It boiled at  $240^{\circ}$  to  $241^{\circ}$  at 748mm.

In order to obtain a product which would not darken on standing, it was found necessary to distill under diminished pressure. At 19mm. it boiled at  $122^{\circ}$  to  $122.5^{\circ}$ , using an Anschütz thermometer.

The yield was 300 grams or 87% of the theoretical.



## Oxidation of Acetomesitylene

90 grams of acetomesitylene, 27 grams of sodium hydroxide, and 270cc. of water were placed in a five-liter balloon flask set in a jar of tap water. The mixture was vigorously stirred by a motor-driven stirrer. When the hydroxide had dissolved and the solution cooled down, 900cc. of water were added, and 180 grams of potassium permanganate put in in small portions. The temperature was kept below 40° by occasionally changing the water in the jar. After about half of the permanganate had been added, 900cc. of water were put in. The addition of the permanganate required about three hours. The solution was stirred for another hour, and then heated on the steam-bath until all of the permanganate had been destroyed. To the hot solution were carefully added 225cc. of 50% sulphuric acid, and the mixture returned to the steam-bath for half an hour. It was then cooled under the tap, and 145 grams of sodium hydroxide added. When the hydroxide had dissolved, the solution was returned to the stirrer, and 500cc. of water added. 230.5 grams of permanganate were added in four portions at half hour intervals. Stirring was continued for three hours. The flask was transferred to the steam-bath, and heated until all of the permanganate was destroyed. To the hot solution were added 700cc. of 50% sulphuric acid and enough sodium bisulphite to destroy all of the oxides of manganese. The solution was quickly filtered by suction, the filtrate being discarded. The precipitate was dissolved in strong ammonia, the solution cooled and shaken out with ether, and filtered by suction. The acid was thrown out by adding sulphuric acid, and filtered hot. It was washed with hot water.

The yield of dry dimethyl terephthallic acid varied from 70 to





95 grams or 65% to 90% in a great number of runs in which there was no apparent difference in procedure.

The acid melts at 298°, using an Anschuetz thermometer.

It is very slightly soluble in hot or cold ether, and insoluble in hot or cold chloroform.

#### Esterification of Dimethyl Terephthallic Acid

150 grams of the dry acid were placed in a flask with 500cc. of absolute methyl alcohol containing 20 grams of dry hydrochloric acid. The solution was boiled under a reflux condenser for five hours. It was then poured, with stirring, into 600cc. of cold water and let stand for about an hour. The liquid was sucked off, and the acid ester washed with water. The filtrates, when cooled in ice, gave a little more good ester.

Titration with standard alkali showed the absence of the neutral ester. Diortho substitution had quantitatively prevented esterification of the second carboxyl.

The yield was over 97%.

The ester melts at 189°-90° with an Anschuetz thermometer.

It is soluble in ether, alcohol, boiling benzene, and glacial acetic acid, but insoluble in cold benzene.

#### Preparation of the Acid Amide.

The ester was dissolved in about twice its weight of strong ammonia, and the solution saturated cold with ammonia. Ammonia was slowly passed in under slightly increased pressure for three or four days. The temperature was maintained at about 45° during this time. The crystalline ammonium salt was then filtered off, sucked dry, washed with cold saturated ammonia followed by ether.





The amide was precipitated from the hot solution of the salt in water by adding acid. The precipitated solution was allowed to stand until cold, filtered, and washed with ether.

The ammoniacal mother liquors were not acidified, but were used to dissolve more ester.

The yield from the first run was only about 25% but was increased to 40% by using the ammoniacal solution a second time.

The mother liquors were finally acidified, and the recovered material treated with methyl alcohol as if it were pure acid. The product was put into ammonia as above.

The yield, after repeated treatment, was about 75% of the theory.

The amide melts at 248° with an Anschuetz thermometer.

It is insoluble in ether, benzene, and chloroform, but soluble in hot water from which it crystallizes on cooling.

It cannot be distilled without decomposition even at 20mm.

#### Iodo Neighboring Acid

The amide was carried through to the iodo acid without isolating any intermediate product.

15.5 grams of finely powdered amide were ground into 180cc. of cold 10% sodium hydroxide solution in a casserole surrounded with ice and salt. A solution of 4.2cc. of bromine in cold sodium hydroxide solution (10%) was added with stirring. The solid matter was allowed to settle, and the liquid decanted. The residue was ground thoroughly and the liquid returned to it. This put all but a negligibly small portion of the amide into solution.

After half an hour's standing the solution was heated for three minutes in a steam-bath, and then quickly heated to boiling



over a free flame. It was cooled under the tap, and the solution transferred to a large beaker setting in ice water. Dilute sulphuric acid was cautiously added until the precipitate, which came out began to redissolve. 50cc. of the dilute acid were then added, and the solution filtered from a very small amount of solid.

The filtrates from two such runs were mixed and cooled to zero. This caused the sulphate to precipitate out. A solution of 20gr. of potassium nitrite in 50cc. of water was then added in four portions at ten-minute intervals. During this treatment the original precipitate dissolved, but another appeared at the last of the process. After standing for fifteen minutes, the mixture was poured into a three-liter balloon flask containing 80 grams of potassium iodide in 200cc. of 25% sulphuric acid. The flask was heated, with occasional shaking, on the steam-bath for forty minutes. It was then cooled under the tap and sufficient bisulphite added to destroy the color.

The iodo acid was filtered off by suction, and washed with bisulphite solution followed with water. No acid could be obtained by extracting the filtrate with ether.

The acid is very soluble in ether.

A great deal of work was done in an attempt to increase the yield of para amino xylic acid by the method of W.A. Noyes (loc.cit.) However, consistent results could not be obtained. In a few runs yields as high as 75% were obtained, but it was found much more satisfactory, both from time and yield, to convert the amino acid to the iodo acid without isolating it.





### Neighboring Xylic Acid

The iodo acid was dissolved in 50cc. of strong ammonia without letting the solution heat up. A few grams of zinc dust were added, and the flask held under the tap for a few minutes. From time to time more zinc was added and the solution shaken. In an hour more zinc and ammonia were added, and the flask placed over the steam-bath so that a temperature of 70° to 80° could be maintained over night. In the morning the zinc was filtered off by suction, and the acid precipitated by adding hydrochloric acid. The solution was shaken out twice with ether, the ether evaporated off, and the residue distilled at 17mm. It distills between 155° and 160°.

The yield, after distilling, was consistently better than 55% of the theory from the amide. It melts at 114°.

Neighboring xylic acid is sparingly soluble in boiling water from which it crystallizes as very fine needles which melt sharply at 116°, using an Anschuetz thermometer.

It is extremely insoluble (when pure) in cold ligroin.

### Reduction of Neighboring Xylic Acid

10 grams of xylic acid were placed in a liter round-bottom flask with 100cc. of dry isoamyl alcohol, and the solution heated to boiling. The flask was specially constructed to carry a large condenser, a mercury-seal motor-driven stirrer, and a tube for admitting pieces of sodium. When boiling had started, pieces of sodium were dropped in, and the stirrer started.

In all, 60 grams of sodium were used. From time to time, more alcohol was added as needed to prevent caking on the bottom of





the flask. The addition of the sodium required about an hour and a half. When all of the sodium had been added, the hot solution was poured into 1500cc. of cold water. As soon as all of the alcoholate was destroyed, the alcohol layer was separated from the solution and placed in a distilling flask with a liter of water and a piece of porous porcelain. Most of the alcohol was distilled off. The solution from which the alcohol layer had been separated was added to the residue in the distilling flask, and all of the alcohol distilled out. The solution began to froth badly as soon as the alcohol was all removed. The residue was cooled, extracted with ether, and acidified. The acidic solution was then extracted with ether; the ether solution dried with sodium sulphate, and placed in the reduction flask. After evaporating off the ether, the reduction was repeated.

In all, the xylic acid was reduced three times. The product was a strong-smelling, semi-solid mass. It was transferred to a small distilling flask, and distilled under reduced pressure. Most of it came over between 154° and 156° at 23mm. A few drops which came over below 130° were discarded.

The distillate was placed in a small flask with 25cc. of hydrobromic acid which had been saturated at zero. The flask was shaken and let stand over night at room temperature. It was then placed near a steam-bath so that the temperature could be held at 40°-45° for a day.

The mixture was then diluted, extracted with ether, and the ether evaporated off in a heavy-walled separatory funnel. Enough saturated carbonate solution was added to dissolve most of the acid. An equal volume of bicarbonate solution was then added, the



funnel placed in cracked ice, and a stirrer introduced. 500 grams of 3% sodium amalgam were added in small portions. From time to time mercury was drawn off so as to give the solution free access to the amalgam. Carbon dioxide was passed into the solution during the addition of the amalgam. It took about twelve hours for the amalgam to liquify. The solution was poured off, the bicarbonate dissolved out of the funnel and added to the main solution, and the whole heated to boiling for a few minutes. After cooling, it was extracted with ether, acidified, again extracted, and the extract once more treated with saturated hydrobromic acid. The acidic product from the second addition of hydrobromic acid, after treatment with amalgam, was dissolved in carbonate solution, and all unsaturation destroyed by adding permanganate to a permanent color. Bisulphite solution was added to destroy oxides of manganese.

The solution was acidified, after it had been extracted with ether. The reduced acid was taken out with ether, the ether removed in a distilling flask, and 200cc. of water added. The solution was distilled until the residue was about 50cc. The solid acid in the distillate was filtered off and dissolved in carbonate solution. The carbonate solution was extracted with ether and then with ligroin, and the hexahydro acid precipitated by adding sulphuric acid.

After filtering off the solid acid (M.P. 71°), the filtrate was combined with the former filtrate and the residue in the distilling flask, and extracted with ether. The extract was added to more xylic acid and reduced.

The yield of good acid was a little more than a gram.





When twice distilled with steam, the acid melts at 73°.

The refractive index is  $n_D^{85}$  1.4340.

It is quite soluble in ligroin.

Several methods were tried out in an endeavor to obtain better yields.

The original method employed in the work was that of W.A. Noyes (loc.cit). 5 grams of xylic acid were dissolved in 20 grams of absolute amyl alcohol, and 10 grams of sodium added in small pieces through a condenser to the boiling solution. More alcohol was added from time to time so as to prevent crust-formation on the sodium. When all of the sodium had been added and used up, the solution was cooled slightly and water added through the condenser. The alcohol was distilled off with steam, the residue acidified with sulphuric acid, and the mixture extracted with ether. The ether was removed by heating under reduced pressure, and the residue again reduced with sodium and amyl alcohol. The acid was reduced three times.

After the third reduction, the acidic product was dissolved in carbonate solution, the solution cooled in ice, and permanganate added to a permanent pink. The oxides of manganese were destroyed with bisulphite, and the solution acidified. Steam distillation gave a white solid which did not melt sharply. A little more was obtained by extracting the distillate. The whole yield was less than a gram.

This method was tried out several times but the yield was never any better.

The next trial was with 6 grams of xylic acid. The acid from



the third reduction with sodium weighed 5.8 grams and had a very disagreeable odor. An attempt was made to fractionate it, but it all came over between 145° and 146° at 15mm. Thinking that it might contain some of the tetrahydro acid with the double union in the 2,3 position, it was boiled with 30% potassium hydroxide solution for an hour. The product did not seem to differ from the original distillate.

It was heated in a sealed tube in the steam-bath with 10 grams of hydrobromic acid (sp.g. 1.78) for fourteen hours. The resulting mixture was cooled and extracted, and the extract dissolved in carbonate solution. The carbonate solution, after extracting with ether, was treated with sodium amalgam according to the method of Aeschan (11). No indifferent substance was obtained. The yield was 2.3 grams melting at 69°.

In order to determine if the alcohol was too dry, a run was made using amyl alcohol to 250cc. of which had been added 1 gram of water. The yield was about a half gram.

A run was made in which 20cc. of absolute ethyl alcohol were added to each 80cc. of amyl alcohol used. The yield was very poor, almost all of the xylic acid being recovered.

Normal butyl alcohol was substituted for amyl alcohol, but the yield was lowered rather than raised.

The next attempt was to add hydrogen catalytically according to the method of Willstatter (12). An apparatus was constructed so that a kjeldahl flask could be vigorously shaken in a water-bath. 5 grams of xylic acid were placed in the flask with 20cc.





of water. The apparatus was warmed and the flask evacuated. Hydrogen was let in, the flask evacuated, and hydrogen again introduced. 0.8 gr. Pt black (freshly prepared) was added, and after evacuating, the apparatus was filled with hydrogen. The gas was put in under slightly increased pressure.

No hydrogen was absorbed in ten hours' shaking in boiling water.

The xylic acid was recovered, and the experiment repeated, using glacial acetic as a solvent. No hydrogen was absorbed.

An attempt was made to reduce the para amino acid by the method of Houben and Pfau (13). 3 grams of the acid were suspended in water and treated as above, using platinum black as catalyst. There was no absorption in 24 hours.

Some acetic acid was added, and shaking continued for five hours without any absorption.

5cc. of hydrochloric acid were added, but no absorption was observed.

3 grams of the amino acid were treated in the same manner as above, using palladium black. There seemed to be a little absorption, but only .3 gram of impure acidic material could be recovered.

1 gram of xylic acid was heated in a bomb in the steam-bath with 1.1 grams sodium, 10cc. amyl alcohol, and some palladium black. As all of the sodium was not used up, the bomb was heated in boiling toluene for three hours. Due to crust on the sodium, not all of it was used up. 1 gram of acid melting at 105° was recovered.

A similar trial was made, using 1 gram of acid, 2.5 grams





sodium, 20cc. amyl alcohol, and some platinum black. All of the xylic acid was recovered.

In a third run, using palladium black, 1 gram of the acid was heated in a bomb with 5 grams sodium and 50cc. of amyl alcohol. There was no reduction.

3 grams of xylic acid were reduced with 30grams of sodium in amyl alcohol, and the product heated in a bomb in the steam-bath with 15 grams of saturated (0%) hydriodic acid for 30 hours. After treating with permanganate in carbonate solution, a small amount of hexahydro acid was obtained.

30 grams of sodium were dropped into 25cc. hot amyl alcohol, and 3 grams of xylic acid, dissolved in 100cc. amyl alcohol, slowly dropped in to the boiling mixture. The sodium coated so badly that more alcohol had to be let in. The method did not give any better yield than the old method of adding the sodium to the alcohol.

On the supposition that the iodo acid might be more susceptible to reduction of the ring at the instant of losing the iodine atom than is xylic acid itself, 8 grams were treated with 25 grams of sodium and amyl alcohol. Almost the theoretical quantity of xylic acid was recovered. On repeating the experiment, substituting normal butyl alcohol for the amyl, no better result was obtained.

The method of Einhorn and Meyerburg (14) was tried on the symmetrical amino xylic acid. 5 grams of the acid were treated in 800 cc. of boiling isoamyl alcohol with 60 grams of sodium in small portions. Throughout the whole treatment a strong test for ammonia could be obtained. No hexahydro xylic was obtained. Some of the



original amino acid was recovered along with a vile smelling oil which was basic in character. No effort was made to identify the substance.

Several attempts were made to reduce the isoamyl ester of xylic acid by the method of Sabatier and Murat (15), using the apparatus of Clarke and Beggs (16) and a specially designed apparatus. The ester was made by the method given in Friedlander (17). It boiled at 155° to 157° at 22mm.

In the first trial 8.5 grams of the ester were put through at 230° in 10 hours. 8.3 grams of material boiling the same as the original were recovered.

New catalyst was prepared, and 8 grams of ester put through at 217°-23° in 6 1/4 hours. .65 grams were recovered. The odor was quite different from that of the original, and more than half of it distilled below 145° at 20 mm. The higher boiling fraction was put through at the same temperature in 6 hours. 3.2 grams were recovered and distilled below 151 at 22mm. The two portions were then batched and put through at 220° in 6 hours. 6 grams of material, of which 3 grams boiled below 150°<sup>25mm.</sup> were obtained.

This fraction was boiled with alcoholic potash for 14 hours. the acid obtained was dissolved in carbonate solution, and treated with permanganate. Less than half of a gram of acid (melting below 60°) was obtained. This was distilled at 18mm., coming over at 142°-44°. The distillate melted at 60°.

The residual ester was boiled with saturated sodium ethylate in alcohol for 4 hours. Only a trace of acid was obtained.

The remaining ester boiled at 140°-45° at 22mm. It was heated near boiling in a long tube with 5 grams of potassium hydroxide





and 2 cc. of water for two hours. There was an odor of amyl alcohol. The acidic product, when cryatallized from glacial formic acid, melted at about 80°.

The residual ester again heated with a paste of potassium hydroxide and water for 18 hours. There was an unmistakable odor of amyl alcohol. An acid was obtained which melted, after several precipitations from alkaline solution, at 103°. It was distilled at 20 mm. A drop of crystalline solid was obtained, It melted at 103°, and would not add bromine in chloroform solution. The chloroform and bromine were evaporated, and the residue still melted at the same point.

An attempt was made to separate the acids obtained from the treatment in amyl alcohol with sodium. It was hoped to avoid destroying so much valuable material with permanganate.

The product from reducing 25 grams of xylic acid in three portions with alcohol and sodium was systematically fractionated at 20mm. It was carried through twenty steps, but no pure substances were obtained. All fractions fell between 146° and 150° at 18-20mm.

8 grams of the above material were placed in a bomb with 8gr. hydriodic acid dissolved in 15 grams of glacial acetic acid, and heated over night in the steam-bath. An acid was obtained which, after several purifications melted at 103°. Titration with .0161 N alkali gave a molecular weight of 156.2, indicating a hexahydro acid.

|                 |       |       |
|-----------------|-------|-------|
| Combustion:     | %C    | %H    |
| Calc. Xylic     | 71.97 | 6.71  |
| Calc. Hexahydro | 69.18 | 10.32 |
| Found           | 69.33 | 9.68  |



An attempt was made to convert the acid to the tetrahydro acid. At the point where the brom acid should have been obtained, was obtained a crystalline substance melting below 140°. Purification by crystallizing from glacial formic acid did not raise the melting point. No hexahydro acid was obtained by treating with alcoholic potash.

Fractional precipitation was next tried, using the product from reducing three times with alcohol and sodium. It was distilled at 23mm. That used distilled between 150° and 160°.

20 grams were dissolved in sodium hydroxide solution, and hydrochloric acid added until the solution became milky. It was extracted twice with ether and treated with four successive portions of four cubic centimeters of concentrated hydrochloric acid. The solution was extracted with ether after the addition of each portion of acid. The last extract proved to be chiefly xylic. The first extract looked like hexahydro xylic, but required a large quantity of permanganate to destroy unsaturation. Some good hexahydro acid ( $N_D^{85} 1.4389$ ) and melting at 73° was obtained.

The second and third fractions were allowed to crystallize and were separated by means of repeated recrystallization from low boiling petroleum ether into two solid acids and an oil. Each of the solids gave an analysis for tetrahydro xylic acid. Each added bromine and reduced permanganate in cold carbonate solution. One of them melted at 93.4° and boiled at 253.5°-254° at 750mm. It gave a refractive index  $N_D^{85} 1.4515$ . The value at 85 was obtained by calculating back from readings taken at 93°, 94°, and 95°.

The other acid was obtained in much smaller quantities. It





melted at 57° and gave a refractive index  $n_D^{85}$  1.4608.

In order to determine the location of the double union in the two acids they were treated with strong potassium hydroxide in iron tubes for twelve hours at the boiling point of the solution. The higher melting acid was recovered entirely unchanged but the lower melting one showed a little higher melting material. Heating the lower melting acid with 25% sodium hydroxide solution at boiling for 24 hours did not give any better results.

Bromine was added to the 93° acid and the product analyzed for bromine.

|  | % Bromine |
|--|-----------|
| Calculated for dibrom tetrahydro xylic | 50.88     |
| Found                                  | 50.43     |

Treatment with 1:1 sulphuric acid gave lactones with both of these acids.

From the above evidence it was decided that the 93° acid was unquestionably one of the 3,4 unsaturated tetrahydro acids.

#### $\Delta_1$ Tetrahydro Neighboring Xylic Acid

This acid was prepared by the method of W.A. Noyes (loc.cit.). 2 grams of the hexahydro acid were treated with 3 grams of phosphorous pentachloride in an open bomb tube held under the tap. When the reaction had slowed down the tube was heated in the steam-bath for a few minutes. It was then cooled, 2.05 grams of bromine introduced and the tube sealed. It was heated in the steam-bath for 3 hours, cooled and opened. The contents were poured into ice water and the mixture extracted with ether. The ether was evaporated off and the oily mass dissolved in boiling glacial formic acid and





the solution boiled under a reflux for an hour. When cool, water was added and the brom acid separated off by means of a small separatory funnel. It was refluxed with alcoholic potash for an hour and a half. Potassium bromide began to separate out before the solution reached boiling. The alcoholic solution was diluted and extracted with ether. Sulphuric acid was then added and the solution again extracted. Steam distilling the extract gave an oil which crystallized on standing.

The yield was poor, not exceeding 20%.

The acid melts at  $90^{\circ}\text{--}91^{\circ}$ , is very slowly soluble in petroleum ether, and has a refractive index  $n_D^{85^{\circ}} 1.4740$

Several attempts were made to obtain the acid in better yields.

The method used by Crossley and Le Sueur (18) was applied to this compound. 2 grams of hexahydro acid were treated with .153 grams of red phosphorous and 4.7 grams of bromine. The product was treated with cracked ice, extracted with ether, dried and then boiled with absolute alcohol to give the brom ester. This was obtained by diluting the alcoholic solution. It was carefully dried, in a bulb with a long tube with 10 cc. diethyl aniline so that the solution was at a temperature of  $160^{\circ}\text{--}165^{\circ}$  for 24 hours. It was then heated up to  $200^{\circ}$  for a half hour. After cooling, excess hydrochloric acid was added and the solution extracted with ether. The residue, after evaporating off the ether, was refluxed several hours with alcoholic potash. Diluting and extracting gave some ester. The solution was acidified with hydrochloric acid, extracted with ether, the ether boiled off, and the residue steam-distilled. A small amount of pure tetrahydro acid was obtained in this manner. The ester was again treated with alcoholic potash for sev-



eral hours but was not entirely saponified. In this way a little more acid was obtained.

A good yield could not be obtained by this method.

An interesting property was discovered in working with the brom acid chloride. It was found that dilute sodium hydroxide did not decompose it even when stirred at room temperature for twelve hours. It was then heated to boiling with 50% potassium hydroxide solution without decomposing the acid chloride. In order to obtain the acid it is necessary to reflux the acid chloride with glacial formic acid for some time. This may account for the poor yields obtained in the preparation of the tetrahydro acid.

#### 1,2 Dibrom Hexahydro Xylic Acid

A weighed amount of the tetrahydro acid was dissolved in chloroform and treated with a little less than the theory of bromine. It became colorless in three hours. More bromine was added and the solution allowed to stand over night. The solvent and excess bromine were aerated off with dry air leaving a white solid which is slightly soluble in ligroin. It has no sharp melting point but decomposes at  $128^{\circ}$  to  $132^{\circ}$  when quickly heated.

It was titrated with N /10 alkali.

.165 grams used 15.3cc.

Theory 5.2

Since three times the theory of alkali is used the bromines must titrate out.

The alkaline solution was acidified with sulphuric acid and extracted with ether. Nitric acid was added to the residue and the solution titrated with N/10 silver nitrate.

Used 9.9cc. Theory 10.4cc.





$\Delta_{1.5}$  Dihydro Neighboring Xylic Acid

The dibrom acid was heated for a half hour on the steam-bath with a slight excess of N/10 alkali. The solution was cooled and extracted with ether. Excess sulphuric acid was added and the solution again extracted. The ether was removed in vacuo, leaving a syrupy acid which was almost entirely soluble in cold carbonate solution. It did not give a test for halogen. The carbonate solution was extracted, acidified, and again extracted. The ether was removed as before and the residue titrated with .0161 N alkali. There was some insoluble residue. This was removed with ether and the acid recovered by acidifying and extracting.

The extract was dissolved in ligroin by warming with a fairly large volume. On evaporating the ligroin in vacuo a white solid was obtained. It melted slowly before the beaker had reached room temperature. The acid was titrated and again gave an appreciable quantity of residue even though the alkaline solution was boiled.

|                                   |            |        |
|-----------------------------------|------------|--------|
| Refractive index before titrating | $n_D^{20}$ | 1.4670 |
| " " after                         | "          | 1.4660 |

|                               |                |
|-------------------------------|----------------|
| Titration:                    | cc. .0161 NaOH |
| 1. Used                       | 112            |
| Theory for dihydro            | 121            |
| Theory for hydroxy tetrahydro | 109            |
| 2. Used                       | 95.8           |
| Theory for dihydro            | 101.8          |
| Theory for hydroxy tetrahydro | 91.9           |

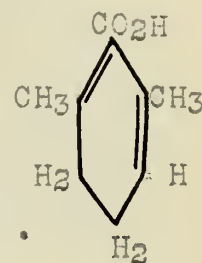
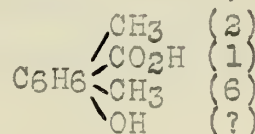
From this data it is evident that the acid is by no means pure



dihydro acid. There are two explanations for the formation of the hydroxy acid. It is formed either by direct substitution of a bromine atom or by addition of water to the dihydro acid. The behavior of the product on titrating seems to point to the second explanation.

| Combustion:                       | % C   | %H   |
|-----------------------------------|-------|------|
| Found                             | 67.65 | 8.10 |
| Calculated for dihydro            | 71.01 | 7.95 |
| Calculated for hydroxy tetrahydro | 63.53 | 8.30 |

The combustion indicates 55-57% of the dihydro acid, and 45-43% of the hydroxy tetrahydro acid,



#### Esterification of Neighboring Xylic Acid

The method employed for the esterification of all of the acids was to dissolve the acid in a large excess of dry methyl alcohol containing 3-4% hydrochloric acid, and reflux for four hours after boiling became vigorous. The most of the alcohol was then boiled off on a steam-bath through a Skinner column. No free acid distilled over in any of the runs. The residue in the flask was cooled and diluted. Sodium carbonate solution was added to strongly alkaline reaction and the solution twice extracted with ether, the extract being washed twice with water and the water returned to the solution. The solution was then shaken out twice with ligroin, acidified with sulphuric acid, and extracted twice with ether. The ether was evaporated off in a beaker and the beaker placed in a vacuum desiccator containing phosphorous pentoxide over



night. It was then weighed, the contents extracted with absolute ether and again weighed.

The difference between the loss in weight and the weight of the sample was recorded as the amount esterified.

|                      | 1        | 2        |
|----------------------|----------|----------|
| Weight of Xylic Acid | 1.000gr. | 1.000gr. |
| " " alcohol          | 65 gr.   | 50gr.    |
| " " HCl              | 2.6gr.   | 1.8gr.   |
| " " xylic recovered  | 0.972gr. | 0.963gr. |
| Acid esterified      | 2.8%     | 3.5%     |

Questioning Rosanoff's view, but hoping to obtain some of the isoamyl ester by direct esterification, the following run was made.

|                             |        |
|-----------------------------|--------|
| Xylic acid                  | 3.6gr. |
| Iso amyl alcohol (B.P.131°) | 100cc. |
| Sulphuric acid              | 2.5cc. |
| Refluxed 64 hours           |        |
| Xylic acid recovered        | 3.4gr. |
| Esterification              | 5.5%   |

#### Esterification of Hexahydro Neighboring Xylic

|                 |       |           |
|-----------------|-------|-----------|
| Hexahydro Xylic | 0.901 | 0.433 gr. |
| Methyl alcohol  | 20    | 20 gr.    |
| HCl             | 0.66  | 0.7 gr.   |
| Acid recovered  | 0.433 | 0.225 gr. |
| Esterification  | 51.9  | 48.0 %    |





Esterification of  $\Delta_1$  Tetrahydro Xylic Acid

|                |       |           |
|----------------|-------|-----------|
| Acid           | 0.620 | 0.421 gr. |
| Methyl alcohol | 20.0  | 20.0 gr.  |
| HCl            | .7    | .7 gr.    |
| Acid recovered | 0.391 | 0.250 gr. |
| Esterification | 36.9  | 40.6 %    |

Esterification of  $\Delta_3$  Tetrahydro Xylic Acid

|                |            |
|----------------|------------|
| Acid           | 0.3092 gr. |
| Methyl alcohol | 20.0 gr.   |
| HCl            | .7 gr.     |
| Acid recovered | 0.0765 gr. |
| Esterification | 75.2 %     |

Esterification of  $\Delta_{1,5}$  Dihydro Xylic Acid \*

|                |           |
|----------------|-----------|
| Acid           | 0.438 gr. |
| Methyl alcohol | 20.0 gr.  |
| HCl            | .7 gr.    |
| Acid recovered | 0.325 gr. |
| Esterification | 25.8 %    |

\* This esterification was run in an atmosphere of hydrogen.



## Conductivity of Neighboring Xylic Acid

The acid was carefully prepared by recrystallizing several times from conductivity water. It melted sharply at 116°.

The cell was standardized against resublimed benzoic, using the values (converted by the factor 1.066) of White and Jones (19).

The solutions were all made up by weight.

Calculations were by the method of Derick (20).

Water  $0.74 \times 10^{-6}$

| C                | $\Lambda_{25^\circ}$ |
|------------------|----------------------|
| N/128            | 91.76                |
| N/256            | 121.9                |
| N/512            | 158.6                |
| N/1024           | 199.1                |
| $\Lambda_0$      | 358                  |
| $K_8^{25^\circ}$ | $69 \times 10^{-5}$  |

## Conductivity of Hexahydro Neighboring Xylic Acid

The acid was purified by repeated steam-distillation from conductivity water in an old Jena glass flask. It melted sharply at 73°.

The acid was found to be very insoluble when suspended in water. Only 4 parts dissolved in 10000 parts of water in six hours at 20°.

Water  $0.89 \times 10^{-6}$

| C      | $\Lambda_{25^\circ}$ |
|--------|----------------------|
| N/512  | 26.6                 |
| N/768  | 32.69                |
| N/1024 | 37.31                |





## Conductivity Hexahydro cont.

|                  |                      |
|------------------|----------------------|
| C                | $\Lambda_{25^\circ}$ |
| N/1536           | 45.39                |
| $\Lambda_0$      | 351                  |
| $K_a^{25^\circ}$ | $1.2 \times 10^{-5}$ |

Conductivity of  $\Delta_1$  Tetrahydro Xylic Acid

Due to the fact that the acid dissolves very slowly, it was thought best to use only the more dilute solutions.

Water  $0.84 \times 10^{-6}$

|                  |                      |
|------------------|----------------------|
| C                | $\Lambda_{25^\circ}$ |
| N/768            | 63.6                 |
| N/1024           | 72.27                |
| N/1536           | 86.08                |
| $\Lambda_0$      | 351                  |
| $K_a^{25^\circ}$ | $5.2 \times 10^{-5}$ |



## VITA

The candidate was born at Chanute, Kansas, August 5, 1892. He graduated from Washington University, St. Louis, in 1915 with the A.B. degree, and obtained the M.A. degree at the University of Illinois in 1917.

While at the University of Illinois the candidate held the appointments, graduate assistant, assistant, and fellow.







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